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THE APPLICATION OF FT-IR REFLECTION-ABSORPTION SPECTROSCOPY FOR DETERMINING THE TEXTURAL PROPERTIES OF COPPER OXIDE THIN FILMS

UPORABA FT-IR REFLEKSIJSKO-ABSORPCIJSKE SPEKTROSKOPIJE ZA DOLOČITEV TEKSTURNIH LASTNOSTI TANKIH PLASTI BAKROVEGA OKSIDA

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Optical CuO coatings were deposited on different substrates with the wet chemistry route using a dip-coating technique. Studies of microstructure with SEM and TEM methods revealed that the films consist of spherical particles with diameters of about 50 nm. It was found that the thicker films exhibit a denser microstructure. From the determination of longitudinal optical modes (LO) of the CuO lattice by FTIR NGIA reflection-absorption spectroscopy and the phenomenon of the Berreman effect a method for qualitative and quantitative determination of the compactness of thin films was developed. The calculation of the optical constants (refractive index and absorption coefficient) for films having different thickness showed that the calculated refractive indices and the frequency shift of the CuO modes depend on the coating thickness and the density of the films. These results are in agreement with the observations of the microstructure and enable a quantitative estimation of the compactness of the CuO coatings.

Keywords: copper oxide, thin films, optical constants, FT-IR NGIA, Berreman effect

Tanke plasti bakrovega(II) oksida smo pripravili po postopku mokre kemije iz bakrovega(II) acetata monohidrata in citronske kisline s tehniko potapljanja. Študij mikrostrukture različno debelih plasti CuO z elektronsko mikroskopijo je pokazal, da so sestavljene iz sferičnih delcev s premerom okrog 50 nm. Pri povečanju debeline smo opazili zgostitev mikrostrukture. Z uporabo FT-IR NGIA refleksijsko-absorpcijske tehnike smo določili longitudinalna LO-nihanja kristalne rešetke CuO in na podlagi Berremanovega pojava razvili metodo za kvalitativno in kvantitativno določitev kompaktnosti strukture tankih plasti. Iz izmerjenih FT-IR NGIA-spektrov različno debelih plasti smo izračunali lomne količnike $n(\lambda)$ in dielektrične funkcije $\varepsilon(\lambda)$, ter ugotovili, da lomni količnik narašča z povečanjem debeline tanke plasti. Dobljeni rezulati potrjujejo ugotovitve študija mikrostrukture in omogočajo kvantitativno ocenitev kompaktnosti tankih plasti bakrovega oksida.

Ključne besede: bakrov oksid, tanke plasti, optične konstante, FT-IR NGIA, Berremanov pojav

1 INTRODUCTION

When infrared radiation impinges on the thin, solid film of a material at near-grazing angles (>70°), in addition to the transversal optical (TO) resonance vibrations, longitudinal optical (LO) modes become visible in the FTIR near-grazing incidence angle (NGIA) spectra. NGIA spectra of films deposited on metal substrates show no more TO modes when p polarized radiation is used. Instead of this the strong reflectivity from the metal substrate decreases at the frequency of the LO mode. This phenomenon is known as the Berreman effect [1]. Harbecke, Heinz and Grosse [2] quantitatively treated the Berreman effect for films deposited on a metal substrate. Relations have been derived, which taking into account the optical constants $n(\lambda)$ and $k(\lambda)$ of film and substrate, give the frequency and intensity of the LO resonance appearing in the NGIA spectra of the film/substrate tandems. In addition to this, it was stated that the Berreman effect also allows investigations of certain qualitative features such as the compactness of thin films.

In order to demonstrate the effect of the film texture on the appearance of the LO resonance modes we undertook spectroscopic investigations of dip-coated CuO films prepared via the sol-gel route using the NGIA spectroscopic technique. Sol-gel-derived CuO films [3,4] exhibit a particulate structure with voids, which are filled in with flocks of the subsequent coat. This makes films that are prepared by multiple dipping more compact in comparison to the films made by single dipping. The objective of this work was to express the compactness of particulate CuO films prepared with various numbers of dippings as a function of the refractive index, $n(\lambda)$, of the corresponding Cu-O stretching modes of the films. Following the method proposed by Nishikida and Hannah [5], the $n(\lambda)$ of the CuO coatings having different thickness were determined and their values correlated with the structural and textural properties.

2 EXPERIMENTAL

2.1. Preparation of sols, gels and thin films - Copper-containing sols were prepared from the cupric acetate precursor using the citric acetate as chelating agent [3,4]. Stable sols became gels after 48 hours at 70 °C. The gel obtained has deep blue color and is an elastic solid. Thin, solid films were prepared by the dip-coating method on glass, and on Al/glass substrates. The lifting speed was 1 cm/min, using a motor-driven unit. Films with dimensions (6.5×2.5×1) cm^3 and (20×10×0.2) cm^3 were prepared. The dipping was repeated several times (up to 30x) in order to increase the thickness of the coating (**Table I**). Glass and aluminized glass substrates were cleaned in ultrasonic bath. As-deposited films were heat treated at 500 °C for 15 minutes.

Table 1: Coating thickness d_N (µm) as a function of the number of dippings (N)
Tabela 1: Debelina tanke plasti d_N (µm) v odvisnosti od števila ciklov potapljanja aluminijeve podlage (N)

Number of dippings (**N**)	Thickness ($\mathbf{d_N}$) (µm)
1	0.0550 ± 0.005
2	0.0896
3	0.1172
6	0.2342
12	0.4276

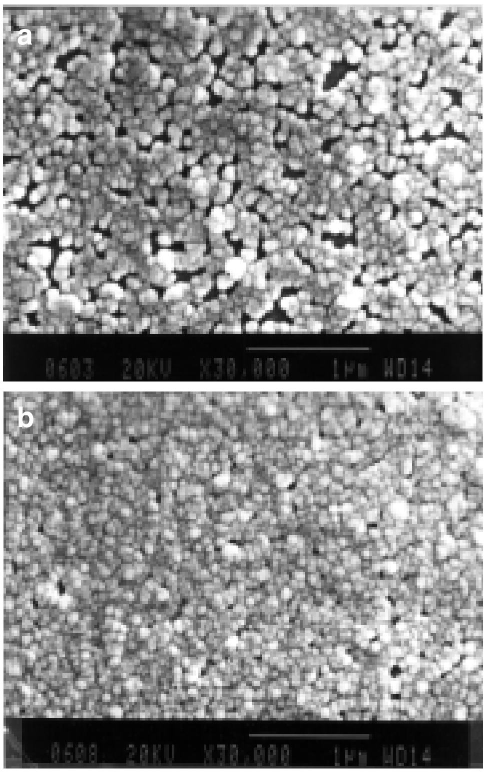

Figure 1: SEM(a,b) micrographs of CuO thin solid coatings: (a) one dipping, 30000x magnification; (b) three dippings, 30000x magnification
Slika 1: Posnetka mikrostrukture tankih plasti CuO z elektronskim mikroskopom: (a) en nanos, 30000-kratna povečava; (b) trije nanosi, 30000-kratna povečava

2.2. Measurement techniques - The SEM and TEM was carried out on a JEOL JXA 840A electron pulse microanalyser. The FT-IR spectra were recorded on a Digilab FTS-80 spectrometer equipped with a Barnes reflection accessory. The measured (NGIA) spectra were obtained at a resolution 8 cm^{-1} by employing 256 scans. Absorbance FT-IR spectra, which were used for the determination of the $k(\lambda)$ values, were measured at a resolution of 8 cm^{-1}.

3 RESULTS AND DISCUSSION

CuO films deposited on glass consist of spherical particles with a diameter of about 55 nm arranged in a well-organized array (**Figure 1a**), which means that films represent optically (no scattering) perfect coatings. The sizes of the voids between particles are about two times the particle diameter. The flocculation of the particles could be about 5-6 particle diameters. Voids, which could be seen on samples prepared by single dipping (**Figure 1a**), are filled in by the particles deposited when the same film is dipped in for the second time. Consequently, repeated dipping increases the thickness and makes the film denser (**Figure 1b**).

In order to interpret the above-mentioned textural features of dip-coated films we measured the NGIA FT-IR spectra of coatings in the spectral range 1200 cm^{-1} - 300 cm^{-1} where Cu-O stretching modes appear (**Figure 2**).

The most significant feature of the NGIA spectra are the frequency shifts and the intensity dependence of the observed LO resonance modes, which these modes exhibit as a function of the coating thickness. The corresponding TO resonance modes appear in the transmission spectra at 535 cm^{-1}, 580 cm^{-1} and 480 cm^{-1}, giving rise to the following LO-TO splitting: $\Delta\lambda$ = 20 cm^{-1}, 45 cm^{-1} and 35 cm^{-1}. The relative change ($\Delta R/R°$)

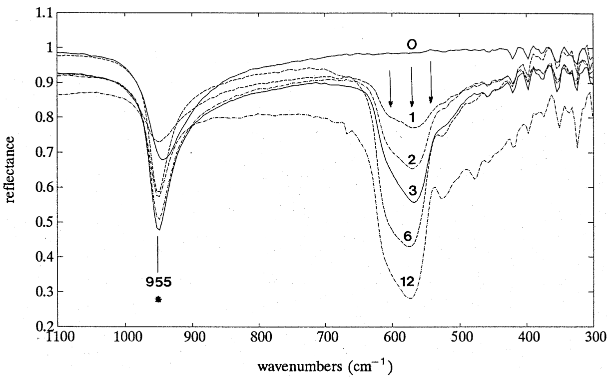

Figure 2: NGIA FT-IR spectra of CuO coatings on Al-substrate (Θ = 80°, 0 = bare Al, 1 - 1x, 2 - 2x, 3 - 3x, 6 - 6x, 12 - 12x dipped substrate). * Indicates Al-O stretching of γ-Al_2O_3
Slika 2: Spektri NGIA FT-IR tankih plasti CuO na aluminijevi podlagi (Θ = 80°, 0 = čisti aluminij; 1, 2, 3, 6, 12 = cikli potaljanja aluminijeve podlage). * Al-O valenčna nihanja γ-Al_2O_3

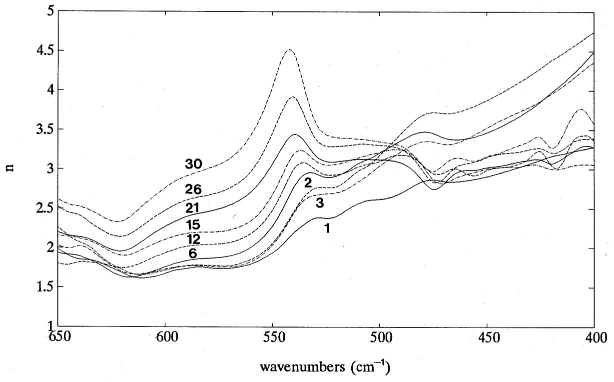

Figure 3: Calculated n(λ) of the CuO coatings. Numbers indicate the number of dippings.

Slika 3: Izračunani lomni količniki $n(\lambda)$ tankih plasti CuO. Številke označujejo število ciklov potapljanja aluminijeve podlage.

of the measured NGIA reflectivity was quantitatively assessed by the following equation (1):

$$\left(\frac{\Delta R}{R_0}\right)=\frac{16\pi nkd\sin^2\Theta}{(n^2+k^2)^2\cos\Theta} \quad (1)$$

For the derivation of $n(\lambda)$ from the above equation, $k(\lambda)$ (the extinction coefficient) was determined from the transmission spectra of the polycrystalline CuO dispersed in the RbJ matrix. The corresponding calculated $n(\lambda)$ revealed that thicker coatings are characterized by larger $n(\lambda)$ values than the thinner ones. It should be noted that the enhancement of $n(\lambda)$ is accompanied by a "blue frequency shift" of the corresponding LO resonances (**Figure 3**).

This phenomenon is of general importance since films prepared by evaporating or ion-plating techniques also exhibit such a behavior when they are deposited under different conditions.

4 CONCLUSIONS

The application of FTIR NGIA spectroscopy and the Berreman effect evaluation enable the quantitative analysis of optical constants of CuO coatings prepared by the dip-coating technique. The increasing refractive index values, $n(\lambda)$, of the CuO coatings showed a strong correlation with the increasing compactness of the multiply dipped coatings. This property is a consequence of the particulate nature of the dip-coated films and confirms their textural and structural features determined with SEM and TEM measurements.

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